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(54) Title: COSMETIC COMPOSITIONS

(57) Abstract

A cosmetic composition is a structured emulsion of a continuous phase containing water-immiscible liquid carrier plus a structurant, and a disperse phase which is a solution of antiperspirant active in a more polar, probably aqueous, solvent. The structurant is a material which forms a network of fibres in the continuous phase, thereby gelling it. The structurant has an enthalpy of gelation in the carrier liquid or a test liquid with a magnitude of at least 30 kJ/mole. This minimum enthalpy of gelation facilitates processing at conveniently accessible temperatures and promotes stability.

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COSMETIC COMPOSITIONS

FIELD OF THE INVENTION

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The present invention relates to cosmetic compositions for application to human skin. Significant forms of the invention are concerned with antiperspirant compositions for application to human skin, especially
10   the axilla. However, the invention can also be applied to other forms of cosmetic composition.

BACKGROUND OF THE INVENTION AND SUMMARY OF PRIOR ART

15   A wide variety of cosmetic compositions for application to human skin make use of a thickened or structured liquid carrier to deliver colour or some other active material to the surface of the skin. A significant example of such cosmetic compositions are
20   antiperspirant compositions which are widely used in order to enable their users to avoid or minimise wet patches on their skin, especially in axillary regions.

Cosmetic compositions have been made in a variety of
25   product forms. One of these is a so-called "stick" which

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Cosmetic compositions have been made in a variety of

25   product forms. One of these is a so-called "stick" which

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is usually a bar of an apparently firm solid material
held within a dispensing container and which retains its
structural integrity and shape whilst being applied.
When a portion of the stick is drawn across the skin
5   surface a film of the stick composition is transferred to
the skin surface. Although the stick has the appearance
of a solid article capable of retaining its own shape for
a period of time, the material usually has a structured
liquid phase so that a film of the composition is readily
10 transferred from the stick to another surface upon
contact. Examples of cosmetic compositions which are, or
can be, marketed in a stick form are lipsticks, lip
salves and eyebrow pencils. The stick form has been used
in particular for deodorant and antiperspirant
15 compositions where the composition includes a deodorant
active material or an antiperspirant active material
respectively.

Another possibility is that a stick is a softer
20 solid composition accommodated in a dispensing container
which in use extrudes the composition through one or more
apertures.

Antiperspirant sticks and other cosmetic
25 compositions can be divided into three categories.

3

Suspension sticks contain a particulate material, notably a particulate antiperspirant active material, suspended in a structured carrier liquid phase. Emulsion sticks normally have a hydrophilic phase forming an emulsion

5   with a second, more hydrophobic, liquid phase. One of the phases contains an active material. Solution sticks typically have the active material dissolved in a structured liquid phase; this phase may be organic solvent or may be a mixture of water and a water-miscible

10   organic solvent. This classification into suspension, emulsion and solution types can be applied to both firm and soft solid compositions.

Besides firm and soft sticks, a number of cosmetic

15   compositions have taken the form of liquids which are formulated to be somewhat viscous and hence pour and flow more slowly than water. One example is antiperspirant compositions in liquid form, such as applied using a roll-on applicator.

20

There is substantial literature on the structuring or thickening of cosmetic compositions which is frequently accomplished using some form of thickening agent as part of the composition.

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Some compositions have a substantial viscosity, which may even make them capable of retaining their own shape for a time, because of transient interactions between molecules of a thickening agent in the liquid.

5

This is characteristic of compositions which are thickened with polymers. Thickening can be attributed to interactions between polymer molecules.

10   It is characteristic of such thickened compositions that their viscosity can be achieved or recovered on standing at room temperature. If subjected to shear their viscosity reduces (hence they are described as shear thinning) but the viscosity recovers towards its

15   original value if the composition is subsequently allowed to stand at room temperature.

Compositions which have two phases, such as emulsions may also have substantial viscosity, even to

20   the extent of being able to sustain their own shape.

Here too it is characteristic of the composition that - provided the composition is stable - its viscosity will recover spontaneously if it is reduced by subjecting

25   the composition to shear.

Compositions have also been given structure and an enhanced viscosity or rigidity by the incorporation of a structurant (also referred to as a gellant or gelling agent) which causes the liquid to gel upon cooling from
5 an elevated temperature.

Gel formation takes place as an exothermic event within a temperature range referred to as the gel point or gel temperature. Upon reheating, melting of the gel
10 takes place as an endothermic event within a temperature range. When the gel melts, the structurant goes into solution in the liquid. Such gels can be disrupted by shearing and do not recover their viscosity for a long time, if at all unless remelted, although a small partial
15 recovery may be observed.

US 4265878, US 4725431, US 4719103 and US 4704271 disclose antiperspirant stick compositions in which a solution of antiperspirant active in aqueous solution is
20 dispersed in a hydrophobic continuous phase of hydrocarbon or silicone oil. This hydrophobic continuous phase is structured to provide a rigid stick by the incorporation of a substantial amount of waxy material, such as stearyl alcohol or spermaceti wax.

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One material which is well known to form gels is 12-hydroxy stearic acid which is discussed in Terech et al "Organogels and Aerogels of Racemic and Chiral 12-hydroxy Octadecanoic Acid", Langmuir Vol 10, 3406-3418,
5   1994. The material is commercially available from Ajinomoto and from Caschem.

US-A-5750096 is one of several documents which teaches that gelation of antiperspirant suspensions can
10   be brought about using esters or amides of 12-hydroxy stearic acid. The alcohol used to form such an ester or the amine used to form such an amide may contain an aliphatic, cycloaliphatic or aromatic group with up to 22 carbons therein. If the group is aliphatic it preferably
15   contains at least three carbon atoms. A cycloaliphatic group preferably contains at least five carbon atoms and may be a fixed ring system such as adamantyl.

WO 98/27954, WO 97/11678 and WO 98/34588 are
20   examples of other documents disclosing the gelation of solutions and suspensions.

N-acyl amino acid amides and esters are also known to structure liquids. We have established that they do
25   so by forming fibrous networks. They are described in US

patent 3969087.   N-Lauroyl-L-glutamic acid di-n-
butylamide is commercially available from Ajinomoto under
their designation GP-1.

5   **SUMMARY OF THE INVENTION**

We have recognised that when a gel is formed, the
solution of the structurant in a liquid may supercool
before gelling commences, and in consequence the gel-
10 melting temperature may be higher than the gel-formation
temperature. If gel-formation takes place in a quiescent
solution of the structurant the extent of supercooling
may be substantial. We have observed that it varies from
one structurant to another.

15

However, if the structurant is being used to prepare
a product where a constituent such as a disperse phase is
mixed into the hot liquid before gel formation, we have
found that it is likely to be necessary to carry out this
20 mixing operation at a temperature at which the
structurant is fully soluble in the liquid. If an
attempt is made to mix the composition at a temperature
at which there is some supercooling, it is likely that
the mixing will induce gelation to commence.

8

It is a consequence of this that when preparing structured liquid compositions containing a structurant to gel the liquid, all constituents of the composition must be subjected to a temperature high enough to
5   dissolve the structuring agent.

We have now found that advantageous properties and processing can be provided in a cosmetic composition which is a structured emulsion, by utilising a gelling
10 agent, in particular a gelling agent of moderate molecular weight, which has an enthalpy of gelation of at least 30 kiloJoule per mole.

According to a first aspect of this invention there
15 is provided a cosmetic composition which is a structured emulsion comprising:

i   a continuous phase containing water-immiscible liquid carrier and a fibre-forming structurant present in the continuous phase, which is effective
20   to gel the composition upon cooling from a temperature at which the structurant is in solution in the carrier liquid, and

ii   a disperse phase which is a solution of antiperspirant active in water, water-soluble
25   solvent or a mixture of them,

characterised in that the structurant has an enthalpy of

gelation in the carrier liquid with a magnitude of at

least 30 kJ/mole,   preferably at least 35 kJ/mole, and

more preferably at least 45kJ/mole, 48 kJ/mole or

5   50 kJ/mole.

The enthalpy of gelation can be determined by

differential scanning calorimetry (DSC).

10   A gelling agent giving an enthalpy of gelation in

this range of at least 30 or 35 kJ/mole upwards can give

the advantage of allowing processing without requiring

the entire composition to be subjected to high

temperature.   This can be valuable in preparing a

15   composition which is an emulsion with a hydrophilic (e.g.

aqueous) disperse phase.   A further advantage resides in

stability of the resulting gel.   These advantages are

more apparent if the enthalpy of gelation is higher (45

kJ per mole or more).

20

By contrast, if the enthalpy of gelation is low, one

or both of two disadvantages are observed.   Rather high

processing temperatures may be needed and/or a gel may be

formed but then undergo unwanted progressive

25   transformation during storage, such as crystals appearing

and growing, softening of the composition or leakage of
liquid from it.

     Although the enthalpy of gelation is a property of
5   the structurant and carrier liquid jointly, we have found
that it is predominantly a property of the structurant.
Consequently, the measurement of enthalpy of gelation in
one or several representative liquids is valuable as
technique (which can be carried out with a small sample
10   and a standard instrument) to assess the suitability of a
potential structurant. It may be desirable to take a
measurement in any one of several representative liquids,
since some structurants do not gel all hydrophobic
carrier liquids.
15

     Therefore in a second aspect this invention provides
a cosmetic composition which is a structured emulsion
comprising
     i)   a continuous phase containing water-immiscible
20   liquid carrier and a fibre-forming structurant
           present in the continuous phase, which is effective
           to gel the composition upon cooling from a
           temperature at which the structurant is in solution
           in the carrier liquid, and
25   ii)   a disperse phase which is a solution of

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antiperspirant active in water, water-soluble

solvent or a mixture of them

characterised in that the structurant is able to gel one

or more of

5   •   decamethyl cyclopentasiloxane

     •   an 80:20 wt% mixture of decamethyl cyclopenta-

          siloxane and isostearyl alcohol

     •   isostearyl alcohol

with an enthalpy of gelation in at least one of the

10   liquids with a magnitude of at least 30 kJ/mole,

preferably at least 35 kJ/mole, more preferably at least

45, 48 or 50 kJ/mole.

A composition according to this invention may take

15   the form of a firm gel with apparent rigidity, or a soft

solid which is able to retain its own shape for a time

(for example if it is taken out of a mould without being

subjected to shear) but which is easily deformed by hand

pressure. Preferred within this invention are

20   compositions which have sufficient rigidity that they can

be regarded as firm solids. The hardness of such

compositions can be measured with a penetrometer, in a

manner which will be described in greater detail below.

25   Certain preferred forms of this invention are

concerned with compositions which are translucent or transparent. As is already known, translucent or transparent compositions can be obtained if it is possible to match the refractive indices of the different
5   constituent phases present in the composition.

We have found that compositions within this invention which are a novel transparent or translucent emulsion can be obtained by formulating the composition
10 to meet two criteria. Firstly the disperse phase and the continuous phase (consisting of the water-immiscible carrier liquid and the structurant contained within that liquid) should be formulated so that their refractive indices match. The refractive index of the continuous
15 phase will be close to the refractive index of the water-immiscible carrier liquid in it. In order to achieve good light transmission through a composition, the refractive index of the water-immiscible continuous phase and the refractive index of the disperse phase should
20 match within 0.003 units preferably 0.002 units.

Secondly, the matched refractive indices of these two phases should lie in a range which is an approximate match to the refractive index of the structurant. The
25 closeness of match required will depend on the

structurant which is used. The refractive index of a
structurant can be determined by making trial
compositions as explained in more detail below. Such
investigation will also show how closely the refractive

5 index of the liquid must be matched to the structurant.

   A composition of this invention will generally be
marketed in a container by means of which it can be
applied at time of use. This container may be of

10 conventional type.

   Another aspect of the invention therefore provides a
cosmetic product comprising a dispensing container having
at least one aperture for delivery of the contents of the

15 container, means for urging the contents of the container
to the said aperture or apertures, and a composition of
either of the previous aspects of the invention in the
container. Preferred is that a composition of this
invention is sufficiently rigid to be accommodated as a

20 stick product in a dispensing container having an open
end at which an end portion of the stick of composition
is exposed for use.

   The compositions of this invention can be produced

25 by processes in which the composition is produced as a

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mobile liquid at an elevated temperature and allowed to cool to permit gel-formation.

Thus, according to a further aspect of the present invention there is provided a process for the production of a cosmetic composition according to the first or second aspect of this invention comprising, not necessarily in any order, the steps of

- incorporating a structurant into a water-immiscible liquid carrier

- mixing the liquid carrier with a disperse liquid phase,

- heating the liquid carrier or a mixture containing it to an elevated temperature at which the structurant is soluble in the water-immiscible liquid carrier,

suitably followed by

- introducing the mixture into a mould which preferably is a dispensing container, and then

- cooling or permitting the mixture to cool to a temperature at which it is thickened or solidified.

In this invention it is possible and indeed preferred that the step of mixing with a disperse phase, and any subsequent steps, are carried out at a

temperature not exceeding 90°C and possibly not exceeding 85°C.

It may be possible to keep below these temperatures

5   throughout the process.

According to a yet further aspect of the present invention, there is provided a method for preventing or reducing perspiration on human skin comprising topically

10 applying to the skin a composition as set forth earlier comprising an antiperspirant active in solution in the disperse phase of the composition, a water-immiscible liquid carrier and a structurant therefor.

15 **DETAILED DESCRIPTION AND PREFERRED EMBODIMENTS**

Measurement of enthalpy of gelation can be carried out using a small sample and standard DSC techniques.

20   Measurement should be carried out at a slow cooling rate and to promote consistency in measurement, it should, if possible, be carried out with the concentration in a standardised range or approximating to a standard value.

25

We have preferred to carry out measurement at a concentration of structurant in the liquid which is not over 8% by weight, preferably from 3%, better 6%, up to

5   8% by weight. Results at such concentrations are generally a close approximation to results at a standardised concentration of 7.5% by weight.

For any structurant which cannot dissolve at such a concentration, an alternative standardised concentration

10 would be 3% by weight.

A gel may first be made by heating and cooling, and a sample of gel sealed in a calorimeter capsule. Alternatively the appropriate weights of liquid and

15 structurant could be sealed in a calorimeter capsule, heated and allowed to cool to a gel in the capsule.

In a preferred procedure a gel is prepared containing from 7 to 7.5% by weight of structuring agent.

20 Approximately 20mg of the gel (for example between 18 and 22 mg) is weighed into a calorimeter capsule and sealed. It is then heated at 10K/minute to a temperature at which the structuring agent is known to be fully soluble in the liquid, held for one minute at this temperature and then

25 a DSC scan is taken while cooling at 2K/minute.

The scan is repeated with a capsule containing
approximately 20mg of decamethyl cyclopentadisiloxane and
in accordance with normal DSC technique, data collected
with the liquid alone (multiplied by a scaling factor if
5   necessary) is subtracted from the data collected with the
gel, so that the gel-formation exotherm appears as a
departure from a flat baseline. The enthalpy is the area
between the peak and the baseline.

10   We have found it appropriate to carry out
measurements, both on the gel and on the liquid alone,
over a broad range of temperatures, such as from -50°C to
+150°C for the sake of accuracy in subtracting one
measurement from the other.
15

For calculation it is assumed that the exotherm
(heat given out during gel formation) comes from the
whole quantity of structuring agent present.

20   Structurant

A number of organic compounds are known to possess
the ability to gel hydrophobic organic liquids such as
water-immiscible hydrocarbon and/or silicone oils by
25   formation of a network of fibres or strands which extends

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throughout the liquid, thereby gelling the liquid. Such

materials are generally non-polymeric, being monomers or

dimers with molecular weight below 10,000 rather than

polymers with more than 8 repeat units or with molecular

5   weight above 10,000.

Materials with this property have been reviewed by

Terech and Weiss in "Low Molecular Mass Gelators of

Organic Liquids and the Properties of their Gels" Chem.

10 Rev 97, 3133-3159 [1997] and by Terech in Chapter 8, "Low-

molecular weight Organogelators" of the book "Specialist

surfactants" edited by I D Robb, Blackie Academic

Professional, 1997.

15   It is characteristic of such structurants that

    o   they are able to gel the organic liquid in the

         absence of any disperse phase

    o   the structured liquids are obtainable by cooling

         from an elevated temperature at which the

20   structurant is in solution in the liquid - this

         solution being mobile and pourable

    o   the structured liquid becomes more mobile if

         subjected to shear or stress

    o   the structure does not spontaneously recover within

25   24 hours if the sheared liquid is left to stand at

room temperature even though a small partial

recovery may be observed

- the structure can be recovered by reheating to a

    temperature at which the structurant is in solution

5 in the liquid, and allowing it to cool back to room

    temperature.

It appears that such structurants operate by

interactions which are permanent unless disrupted by

10 shear or heating. Such structurants operate by forming a

network of strands or fibres extending throughout the

gelled liquid. In some cases these fibres can be

observed by electron microscopy, although in other cases

the observation of the fibres which are believed to be

15 present is prevented by practical difficulties in

preparing a suitable specimen. When observed, the fibres

in a gel are generally thin (diameter less than 0.5μ,

often less than 0.2μ) and appear to have numerous

branches or interconnections.

20

From our observations made using differential

scanning calorimetry we believe that fibrous networks

consist of crystalline material. The crystalline fibres

may or may not be the same polymorph as macroscopic

25 crystals obtained by conventional crystallization from a

20

solvent.

A novel structurant which is the subject of a co-
pending application and which may be used in this
invention is an ester of cellobiose and a fatty acid,
preferably of 6 to 13 carbon atoms especially 8 to 11
carbon atoms. Preferably the cellobiose is fully
esterified, or nearly so, and is in the
α-anomeric form.

The structure of such a compound in its α-anomeric
form is:
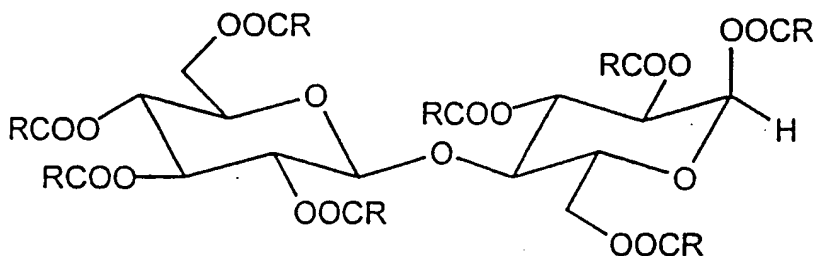
where R is an alkyl or alkenyl chain of 5 to 12 carbon
atoms so that the acyl group contains 6 to 13 carbon
atoms. Particularly preferred acyl groups incorporate a
linear alkyl chain of 7 to 10 carbon atoms and are thus
octanoyl, nonanoyl, decanoyl or undecanoyl.

21

The acyl groups may have a mixture of chain lengths
but it is preferred that they are similar in size and
structure. Thus it is preferred that all of the acyl
groups are aliphatic and at least 90% of the acyl groups

5   have a chain length within a range such that the shorter
and longer chain lengths in the range differ by no more
than two carbon atoms, i.e. length in a range from m - 1
to m + 1 carbon atoms where the mean acyl chain length m
has a value in a range from 7 to 10 or 11. Commercially

10 available feedstocks for these acyl groups are likely to
include a small percentage of acyl groups which differ
from the majority and may have a branched rather than
linear chain. Thus it is likely that more than 90% but
less than 100% of the acyl groups will meet the desired

15 criterion of chain lengths in a range from m - 1 to m + 1
carbon atoms.

Linear aliphatic acyl groups may be obtained from
natural sources, in which case the number of carbon atoms

20 in the acyl group is likely to be an even number or may
be derived synthetically from petroleum as the raw
material in which case both odd and even numbered chain
lengths are available.

25   Synthetic methods for the esterification of

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saccharides are well known. The esterification of
cellobiose has been reported by Takada et al in *Liquid
Crystals*, (1995) Volume 19, pages 441-448. This article
gives a procedure for the production of the alpha anomers

5   of cellobiose octa-alkanoates by esterification of β-
cellobiose using an alkanoic acid together with
trifluoracetic anhydride.

For this invention the structurant mnay be an
10 esterified saccharide as discussed above but selected so
that it also satisfies the criterion of an enthalpy of
gelation of at least 30, preferably at least 45,
kilojoule per mole.

15 **Carrier liquid**

The water-immiscible carrier liquid in the
continuous phase comprises one or a mixture of materials
which are relatively hydrophobic so as to be immiscible
20 in water. Some hydrophilic liquid may be included in the
carrier, provided the overall carrier liquid mixture is
immiscible with water. It will generally be desired that
this carrier is liquid (in the absence of structurant) at
temperatures of 15°C and above. It may have some
25 volatility but its vapour pressure will generally be less

than 4 kPa (30mmHg) at 25°C so that the material can be
referred to as an oil or mixture of oils. More
specifically, it is desirable that at least 80% by weight
of the hydrophobic carrier liquid should consist of
5   materials with a vapour pressure not over this value of 4
kPa at 25°C.

It is preferred that the hydrophobic carrier
material includes a volatile liquid silicone, i.e. liquid
10   polyorganosiloxane. To class as "volatile" such material
should have a measurable vapour pressure at 20 or 25°C.
Typically the vapour pressure of a volatile silicone lies
in a range from 1 or 10 Pa up to 2 kPa at 25°C.

15   It is desirable to include volatile silicone because
it gives a "drier" feel to the applied film after the
composition is applied to skin.

Volatile polyorganosiloxanes can be linear or cyclic
20   or mixtures thereof. Preferred cyclic siloxanes include
polydimethsiloxanes and particularly those containing
from 3 to 9 silicon atoms and preferably not more than 7
silicon atoms and most preferably from 4 to 6 silicon
atoms, otherwise often referred to as cyclomethicones.
25   Preferred linear siloxanes include polydimethylsiloxanes

24

containing from 3 to 9 silicon atoms. The volatile

siloxanes normally by themselves exhibit viscosities of

below 10^{-5} m^2/sec (10 centistokes), and particularly above

10^{-7} m^2/sec (0.1 centistokes), the linear siloxanes

5   normally exhibiting a viscosity of below 5 x 10^{-6} m^2/sec (5

centistokes). The volatile silicones can also comprise

branched linear or cyclic siloxanes such as the

aforementioned linear or cyclic siloxanes substituted by

one or more pendant $-0-Si(CH_3)_3$ groups. Examples of

10   commercially available silicone oils include oils having

grade designations 344, 345, 244, 245 and 246 from Dow

Corning Corporation; Silicone 7207 and Silicone 7158 from

Union Carbide Corporation; and SF1202 from General

Electric.

15

The hydrophobic carrier employed in compositions

herein can alternatively or additionally comprise non-

volatile silicone oils, which include polyalkyl siloxanes,

polyalkylaryl siloxanes and polyethersiloxane copolymers.

20   These can suitably be selected from dimethicone and

dimethicone copolyols. Commercially available non-

volatile silicone oils include Dow Corning 556 and Dow

Corning 200 series.

25   The water-immiscible liquid carrier may contain from

0 to 100% by weight of one or more liquid silicones.
Preferably, there is sufficient liquid silicone to provide
at least 10%, better at least 15%, by weight of the whole
composition. If silicone oil is used, volatile silicone

5 preferably lies in a range from 20% possibly from 30 or
40% up to 100% of the weight of the water-immiscible
carrier liquid. In many instances, when a non-volatile
silicone oil is present, its weight ratio to volatile
silicone oil is chosen in the range of from 1:3 to 1:40.

10

Silicon-free hydrophobic liquids can be used instead
of, or more preferably in addition to liquid silicones.
Silicon-free hydrophobic organic liquids which can be
incorporated include liquid aliphatic hydrocarbons such as

15 mineral oils or hydrogenated polyisobutene, often selected
to exhibit a low viscosity. Further examples of liquid
hydrocarbons are polydecene and paraffins and isoparaffins
of at least 10 carbon atoms.

20   Other hydrophobic carriers are liquid aliphatic or
aromatic esters.

Suitable aliphatic esters contain at least one long
chain alkyl group, such as esters derived from C_1 to C_{20}

25 alkanols esterified with a C_8 to C_{22} alkanoic acid or C_6

to C_{10} alkanedioic acid. The alkanol and acid moieties or mixtures thereof are preferably selected such that they each have a melting point of below 20°C. These esters include isopropyl myristate, lauryl myristate, isopropyl
5   palmitate, diisopropyl sebacate and diisopropyl adipate.

Suitable liquid aromatic esters, preferably having a melting point of below 20°C, include fatty alkyl
10 benzoates. Examples of such esters include suitable C_8 to C_{18} alkyl benzoates or mixtures thereof.

Further instances of suitable hydrophobic carriers comprise liquid aliphatic ethers derived from at least
15 one fatty alcohol, such as myristyl ether derivatives e.g. PPG-3 myristyl ether or lower alkyl ethers of polyglycols such as PPG-14 butyl ether.

Aliphatic alcohols which are solid at 20°C, such as
20 stearyl alcohol are preferably absent or present in low concentration such as less than 5% by weight of the whole composition since these lead to visible white deposits when a composition is used.

25   However, aliphatic alcohols which are liquid at 20°C

may be employed. These include branched chain alcohols
of at least 10 carbon atoms such as isostearyl alcohol
and octyl dodecanol.

5   Very polar materials are preferably excluded or
present in only small quantity in the water-immiscible
carrier liquid. Preferably therefore, this liquid or
mixture of liquids contains not more than 10% of its own
weight, better not more than 5%, of any constituent which
10   is a water-miscible compound.

         Silicon-free liquids can constitute from 0-100% of
the water-immiscible liquid carrier, but it is preferred
that silicone oil is present and that the amount of
15   silicon-free constituents preferably constitutes up to 50
or 60% and in many instances from 10 or 15% up to 50 or
60% by weight of the carrier liquid.

         If any oxygen-containing silicon-free organic
20   liquids are included in the hydrophobic carrier liquid,
the amount of them is likely to be not over 70% by weight
of the carrier liquid. Smaller amounts, ranging up to
20, 30 or 35% by weight are likely.

25   The carrier liquid must be compatible with the

structurant. If the structurant is too soluble or conversely is very insoluble in the carrier liquid it may fail to form a gel and the carrier liquid should be modified to alter its polarity.

5

Liquid Disperse Phase

A composition of this invention is an emulsion which contains a polar disperse phase. The disperse phase may
10 be a solution of an active ingredient.

The hydrophilic disperse phase in an emulsion normally comprises water as solvent and can comprise one or more water soluble or water miscible liquids in
15 addition to or replacement for water. The proportion of water in an emulsion according to the present invention is often selected in the range of up to 60%, and particularly from 10% up to 40% or 50% of the whole formulation.

20

One class of water soluble or water-miscible liquids comprises short chain monohydric alcohols, e.g. C_1 to C_4 and especially ethanol or isopropanol, which can impart a deodorising capability to the formulation. A further
25 class of hydrophilic liquids comprises diols or polyols

preferably having a melting point of below 40°C, or which
are water miscible. Examples of water-soluble or water-
miscible liquids with at least one free hydroxy group
include ethylene glycol, 1,2-propylene glycol, 1,3-
5   butylene glycol, hexylene glycol, diethylene glycol,
dipropylene glycol, 2-ethoxyethanol, diethylene glycol
monomethylether, triethyleneglycol monomethylether and
sorbitol. Especially preferred are propylene glycol and
glycerol.

10

In an emulsion the disperse phase is likely to
constitute from 5 to 80 or 85% of the weight of the
composition preferably from 5 to 50 or 65% more
preferably from 25 or 35% up to 50 or 65%, while the
15   continuous phase with the structurant therein provides
the balance from 15 or 35% up to 95% of the weight of the
composition. Compositions with a high proportion of
disperse phase i.e. from 65 to 85% disperse phase may be
advantageous because the large proportion of disperse
20   phase can make a contribution to hardness.

An emulsion composition will generally include one
or more emulsifying surfactants which may be anionic,
cationic, zwitterionic and/or nonionic surfactants. The
25   proportion of emulsifier in the composition is often

selected in the range up to 10% by weight and in many
instances from 0.1 or 0.25 up to 5% by weight of the
composition. Most preferred is an amount from 0.1 or
0.25 up to 3% by weight. Nonionic emulsifiers are

5   frequently classified by HLB value. It is desirable to
use an emulsifier or a mixture of emulsifiers with an
overall HLB value in a range from 2 to 10 preferably from
3 to 8.

10   It may be convenient to use a combination of two or
more emulsifiers which have different HLB values above
and below the desired value. By employing the two
emulsifiers together in appropriate ratio, it is readily
feasible to attain a weighted average HLB value that

15   promotes the formation of an emulsion.

      Many suitable emulsifiers of high HLB are nonionic
ester or ether emulsifiers comprising a polyoxyalkylene
moiety, especially a polyoxyethylene moiety, often

20   containing from about 2 to 80, and especially 5 to 60
oxyethylene units, and/or contain a polyhydroxy compound
such as glycerol or sorbitol or other alditol as
hydrophilic moiety. The hydrophilic moiety can contain
polyoxypropylene. The emulsifiers additionally contain a

25   hydrophobic alkyl, alkenyl or aralkyl moiety, normally

containing from about 8 to 50 carbons and particularly

from 10 to 30 carbons. The hydrophobic moiety can be

either linear or branched and is often saturated, though

it can be unsaturated, and is optionally fluorinated.

5   The hydrophobic moiety can comprise a mixture of chain

lengths, for example those deriving from tallow, lard,

palm oil, sunflower seed oil or soya bean oil. Such

nonionic surfactants can also be derived from a

polyhydroxy compound such as glycerol or sorbitol or

10   other alditols. Examples of emulsifiers include

ceteareth-10 to -25, ceteth-10-25, steareth-10-25 (i.e.

C16 to C18 alcohols ethoxylated with 10 to 25 ethylene

oxide residues) and PEG-15-25 stearate or distearate.

Other suitable examples include C_{10}-C_{20} fatty acid mono,

15   di or tri-glycerides. Further examples include C_{18}-C_{22}

fatty alcohol ethers of polyethylene oxides (8 to 12 EO).

Examples of emulsifiers, which typically have a low

20   HLB value, often a value from 2 to 6 are fatty acid mono

or possibly diesters of polyhydric alcohols such as

glycerol, sorbitol, erythritol or trimethylolpropane.

The fatty acyl moiety is often from C_{14} to C_{22} and is

saturated in many instances, including cetyl, stearyl,

25   arachidyl and behenyl. Examples include monoglycerides

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of palmitic or stearic acid, sorbitol mono or diesters of
myristic, palmitic or stearic acid, and
trimethylolpropane monoesters of stearic acid.

5   A particularly desirable class of emulsifiers
comprises dimethicone copolymers, namely polyoxyalkylene
modified dimethylpolysiloxanes. The polyoxyalkylene
group is often a polyoxyethylene (POE) or
polyoxypropylene (POP) or a copolymer of POE and POP.
10 The copolymers often terminate in C_1 to C_{12} alkyl groups.

        Suitable emulsifiers and co-emulsifiers are widely
available under many trade names and designations
including Abil™, Arlacel™, Brij ™, Cremophor™, Dehydrol™,
15 Dehymuls™, Emerest ™, Lameform™, Pluronic™, Prisorine™,
Quest PGPR™, Span ™, Tween ™, SF1228, DC3225C and Q2-
5200.

Antiperspirant Actives

20

        Antiperspirant actives, are preferably incorporated
in an amount of from 0.5-60%, particularly from 5 to 30%
or 40% and especially from 5 or 10% to 30 or 35% of the
weight of the whole composition.

25

33

·Antiperspirant actives for use herein are often

selected frcm astringent active salts, including in

particular aluminium, zirconium and mixed

aluminium/zirconium salts, including both inorganic

5   salts, salts with organic anions and complexes. Preferred

astringent salts include aluminium, zirconium and

aluminium/zirconium halides and halohydrate salts, such

as chlorohydrates.

10   Aluminium halohydrates are usually defined by the

general formula $Al_2(OH)_xQ_y.wH_2O$ in which Q represents

chlorine, bromine or iodine, x is variable from 2 to 5

and x + y = 6 while wH_2O represents a variable amount of

hydration. Especially effective aluminium halohydrate

15   salts, known as activated aluminium chlorohydrates, are

described in EP-A-6739 (Unilever NV et al), the contents

of which specification is incorporated herein by

reference. Some activated salts do not retain their

enhanced activity in the presence of water but are useful

20   in substantially anhydrous formulations, i.e.

formulations which do not contain a distinct aqueous

phase.

Zirconium actives can usually be represented by the

25   empirical general formula: $ZrO(OH)_{2n-nz}3_z.wH_2O$ in which z

is a variable in the range of from 0.9 to 2.0 so that the
value 2n-nz is zero or positive, n is the valency of B,
and B is selected from the group consisting of chloride,
other halide, sulphamate, sulphate and mixtures thereof.

5   Possible hydration to a variable extent is represented by
wH_2O. Preferable is that B represents chloride and the
variable z lies in the range from 1.5 to 1.87. In
practice, such zirconium salts are usually not employed
by themselves, but as a component of a combined aluminium

10   and zirconium-based antiperspirant.

The above aluminium and zirconium salts may have
coordinated and/or bound water in various quantities
and/or may be present as polymeric species, mixtures or

15   complexes. In particular, zirconium hydroxy salts often
represent a range of salts having various amounts of the
hydroxy group. Zirconium aluminium chlorohydrate may be
particularly preferred.

20   Antiperspirant complexes based on the above-
mentioned astringent aluminium and/or zirconium salts can
be employed. The complex often employs a compound with a
carboxylate group, and advantageously this is an amino
acid. Examples of suitable amino acids include dl-

25   tryptophan, dl-β-phenylalanine, dl-valine, dl-methionine

and β-alanine, and preferably glycine which has the
formula $CH_2(NH_2)COOH$.

It is highly desirable to employ complexes of a

5   combination of aluminium halohydrates and zirconium
chlorohydrates together with amino acids such as glycine,
which are disclosed in US-A-3792068 (Luedders et al).
Certain of those Al/Zr complexes are commonly called ZAG
in the literature. ZAG actives generally contain

10   aluminium, zirconium and chloride with an Al/Zr ratio in
a range from 2 to 10, especially 2 to 6, an Al/Cl ratio
from 2.1 to 0.9 and a variable amount of glycine.
Actives of this preferred type are available from
Westwood, from Summit and from Reheis.

15

Other actives which may be utilised include
astringent titanium salts, for example those described in
GB 2299506A.

20   The antiperspirant active will be dissolved in the
disperse phase. In this case, the antiperspirant active
will often provide from 3 to 60% by weight of the aqueous
disperse phase, particularly from 10% or 20% up to 55% or
60% cf that phase. The weight of antiperspirant active

25   does not include any water of hydration which may be

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present in the solid active before it is dissolved.

Optional ingredients

5   Optional ingredients in compositions of this

invention can include deodorants, for example at a

concentration of up to about 10% w/w. Suitable deodorant

actives can comprise deodorant effective concentrations

of antiperspirant metal salts, deoperfumes, and/or

10   microbicides, including particularly bactericides, such

as chlorinated aromatics, including biguanide

derivatives, of which materials known as Irgasan DP300 ™,

(Triclosan), Tricloban ™, and Chlorhexidine warrant

specific mention. A yet another class comprises

15   biguanide salts such as available under the trade mark

Cosmosil ™.

Other optional ingredients include wash-off agents,

often present in an amount of up to 10% w/w to assist in

20   the removal of the formulation from skin or clothing.

Such wash-off agents are typically nonionic surfactants

such as esters or ethers containing a C_8 to C_{22} alkyl

moiety and a hydrophilic moiety which can comprise a

polyoxyalkylene group (POE or POP) and/or a polyol.

25

A further optional constituent of the formulation
comprises one or more secondary structurants which can be
employed in addition to the esterified saccharide which
is the primary structurant. The amount of such secondary
5 structurants in the formulation is often zero, and
usually not more than 15% of the formulation. It is
normally not greater than the amount of the primary
structurant.

10 The secondary structurants employable herein can be
non-polymeric or polymeric. Solid linear fatty alcohol
and/or a wax may be included but are not preferred. Non-
polymeric secondary structurants, perhaps gelling agents
of lower gel formation enthalpy, can be included.
15 Gellants can comprise dibenzylidene alditols, e.g.
dibenzylidene sorbitol. Further suitable gellants can
comprise lanosterol, selected N-acyl amino acid
derivatives, including ester and amide derivatives, such
as N-lauroyl glutamic acid dibutylamide, which gellants
20 can be contemplated in conjunction with 12-hydroxy
stearic acid or an ester or amide derivative thereof.
Still further gellants include amide derivatives of di or
tribasic carboxylic acids, such as alkyl N,N'
dialkylsuccinamides, e.g. dodecyl N,N'-
25 dibutylsuccinamide.

Polymeric structurants which can be employed can
comprise organo polysiloxane elastomers such as reaction
products of a vinyl terminated polysiloxane and a cross
linking agent or alkyl or alkyl polyoxyalkylene-
5   terminated poly (methyl substituted) or poly (phenyl
substituted) siloxanes. A number of polyamides have also
been disclosed as structurants for hydrophobic liquids.
Polymers containing both siloxane and hydrogen bonding
groups, which might be used as secondary structurants,
10   have been disclosed in WO 97/36572 and WO 99/06473. If
an aqueous disperse phase is present, Polyacrylamides,
polyacrylates or polyalkylene oxides may be used to
structure or thicken this aqueous phase.

15   The compositions herein can incorporate one or more
cosmetic adjuncts conventionally contemplatable for
antiperspirant solids or soft solids. Such cosmetic
adjuncts can include skin feel improvers, such as talc or
finely divided polyethylene, for example in an amount of
20   up to about 10%; skin benefit agents such as allantoin or
lipids, for example in an amount of up to 5%; colours;
skin cooling agents other than the already mentioned
alcohols, such a menthol and menthol derivatives, often
in an amount of up to 2%, all of these percentages being
25   by weight of the composition. A commonly employed

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adjunct is a perfume, which is normally present at a
concentration of from 0 to 4% and in many formulations
from 0.25 to 2% by weight of the composition.

5   **Translucent/Transparent Compositions**

It is possible to construct the formulation of an
emulsion such that the emulsion is translucent or
transparent. In order to do this the refractive indices
10   of the water-immiscible continuous phase and the polar or
aqueous disperse phase must be matched to each other and
the value of refractive index at which they are matched
must also approximately match the refractive index of the
structurant.

15

The refractive index of a fibrous network of a
structurant can be determined by using that structurant
to gel a number of oils or oil mixtures of differing
refractive index. When the resulting gel is transparent,
20   the refractive index of the oil or oil mixture(which can
be determined by conventional measurement) is a good
approximation to the refractive index of the structurant.
The oils or mixtures or oils should be chosen from these
which are gelled well by the structurant to avoid
25   interfering effects. When the gel is not transparent,

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but is translucent, it will indicate a refractive index
which is not precisely matched to the refractive index of
the structurant, and thus indicate an amount of mismatch
which can be tolerated without loss of translucency. It
5   is likely that the matched refractive indices of the
liquid phases will be not over 0.07 units below and not
over 0.04 units above the refractive index of the
structurant.

10   Using this method we have determined the refractive
index of a preferred structurant, namely cellobiose octa-
nonanoate, to fall in a range between 1.45 and 1.50,
being approximately 1.48 at 22°C. With this structurant
we have found that the value at which the refractive
15   indices of the continuous and disperse phases are matched
can be somewhat below the refractive index of the
structurant, down to a value of 1.42 or even down as far
as 1.41 or 1.40. A value slightly above 1.48 would be
useable also, but is inconvenient to achieve.
20

     For the continuous phase, silicon-free water-
immiscible liquid oils generally have refractive indices
in a range from 1.43 to 1.49 at 22°C and can be used
alone or mixed together to give a silicon-free carrier
25   liquid with refractive index in this range. Volatile

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silicone oils generally have a refractive index slightly

below 1.40 at 22°C, but carrier liquid mixtures with

refractive indices in the range from 1.41 to 1.46 can be

obtained by mixing volatile silicone with other oils.

5   Non-volatile silicone oils generally have refractive

indices in a range from 1.45 to 1.48 at 22°C and so can

be included when desired.

The RI of the continuous phase will be very close to

10 the RI of the carrier liquid (usually a carrier liquid

mixture) which is its principal component.

For the disperse phase, a solution of an

antiperspirant active salt in water alone will generally

15 display a refractive index below 1.425. The refractive

index can be raised by incorporating a diol or polyol

into the aqueous solution. It is believed to be novel to

match the refractive index of a polar disperse phase to

that of a structurant network within a continuous phase.

20 Moreover, it can be achieved without using so much diol

or polyol as will make the composition excessively

sticky.

For the regular production of compositions with

25 optimum transparency it may prove desirable to monitor

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the refractive indices of the raw materials to detect any

batch to batch variation. If necessary the composition

of a liquid phase can be adjusted by variation of the

quantity of a constituent material.

5

Mechanical Properties and Product Packages

The compositions of this invention are structured

liquids and may be firm or soft in appearance. Even a

10 soft solid has an ability to sustain its own shape, for

instance if it is removed from a mould without being

subjected to shear it will retain its shape for at least

30 seconds, usually longer.

15   A composition of this invention will usually be

marketed as a product comprising a container with a

quantity of the composition therein, where the container

has at least one aperture for the delivery of

composition, and means for urging the composition in the

20 container towards the delivery aperture. Conventional

containers take the form of a barrel of oval cross

section with the delivery aperture(s) at one end of the

barrel.

25   A composition of this invention may be sufficiently

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rigid that it is not apparently deformable by hand
pressure and is suitable for use as a stick product in
which a quantity of the composition in the form of a
stick is accommodated within a container barrel having an
5   open end at which an end portion of the stick of
composition is exposed for use. The opposite end of the
barrel is closed.

Generally the container will include a cap for its
10 open end and a component part which is sometimes referred
to as an elevator or piston fitting within the barrel and
capable of relative axial movement along it. The stick
of composition is accommodated in the barrel between the
piston and the open end of the barrel. The piston is
15 used to urge the stick of composition along the barrel.
The piston and stick of composition may be moved axially
along the barrel by manual pressure on the underside of
the piston using a finger or rod inserted within the
barrel. Another possibility is that a rod attached to
20 the piston projects through a slot or slots in the barrel
and is used to move the piston and stick. Preferably the
container also includes a transport mechanism for moving
the piston comprising a threaded rod which extends
axially into the stick through a correspondingly threaded
25 aperture in the piston, and means mounted on the barrel

for rotating the rod. Conveniently the rod is rotated by means of a handwheel mounted on the barrel at its closed end, i.e. the opposite end to the delivery opening.

5   If a composition of this invention is softer, but still capable of sustaining its own shape it will be more suited for dispensing from a barrel with a closure instead of an open end, where the closure has one or more apertures through which composition from the barrel can

10   be extruded. The number and design of such apertures is at the discretion of the designer of the package.

The component parts of such containers are often made from thermoplastic materials, for example

15   polypropylene or polyethylene. Descriptions of suitable containers, some of which include further features, are found in US patents 4865231, 5000356 and 5573341.

Measurement of Properties

20   i) Penetrometer

The hardness and rigidity of a composition which is a firm solid can be determined by penetrometry. If the composition is a softer solid, this will be observed as a substantial lack of any resistance to the penetrometer

25   probe.

45

A suitable procedure is to utilises a lab plant PNT
penetrometer equipped with a Seta wax needle (weight 2.5
grams) which has a cone angle at the point of the needle
specified to be 9°10′ ± 15′. A sample of the composition
5   with a flat upper surface is used. The needle is lowered
onto the surface of the composition and then a
penetration hardness measurement is conducted by allowing
the needle with its holder to drop under a total weight,
(i.e. the combined weight of needle and holder) of 50
10   grams for a period of five seconds after which the depth
of penetration is noted.

Desirably the test is carried out at a number of
points on each sample and the results are averaged.
15   Utilising a test of this nature, an appropriate hardness
for use in an open-ended dispensing container is a
penetration of less than 30 mm in this test, for example
in a range from 2 to 30 mm. Preferably the penetration
is in a range from 5mm to 20 mm.
20

In a specific protocol for this test measurements on
a stick were performed in the stick barrel. The stick
was wound up to project from the open end of the barrel,
and then cut off to leave a flat, uniform surface. The
25   needle was carefully lowered to the stick surface, and

then a penetration hardness measurement was conducted.
This process was carried out at six different points on
the stick surface. The hardness reading quoted is the
average value of the 6 measurements.

5

ii) Texture analyser

The hardness of a softer solid can be measured by
using a texture analyser. This test apparatus can move a
blunt probe into or out from a sample at a controlled
10 speed and at the same time measure the applied force.
The parameter which is determined as hardness is a
function of the peak force and the projected area of
indentation.

15   A specific test protocol used a Stable Micro systems
TA.XT2i Texture Analyser. A metal sphere, of diameter
9.5mm, was attached to the underside of the *Texture
Analyser's* 5 kg load cell such that it could be used for
indenting a sample placed beneath it on the base plate of
20 the instrument. After positioning the sample, the sphere
position was adjusted until it was just above the sample
surface. *Texture Expert Exceed* software was used to
generate the subsequent motion profile used in the test
method. This profile initially indented the sphere into
25 the sample at an indentation speed of 0.05mm/s until a

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designated force was reached, which was chosen such that
the distance of penetration into the sample was less than
the radius of the sphere. At this load the direction of
motion of the sphere was immediately reversed to withdraw
5   the sphere from the sample at the same speed of 0.05mm/s.
During the course of the test, the data acquired were
time(s), distance (mm) and force (N) and the data
acquisition rate was 25 Hz.

10   Suitable samples for measurement were either
contained in stick barrels, which had a screw mechanism,
or in 15 ml glass jars. For the barrel samples, the
stick was wound up until it protruded above the edges of
the barrel and then a knife was used to skim the top of
15 the barrel in such a way as to leave a flat uniform
surface. The stick was then pushed back into the barrel
as far as possible to minimise any mechanical
interference resulting from the compliance of the screw
mechanism in the pack. Two indents were generally made
20 either side of the screw. The samples in the 15 ml jars
needed no surface preparation but only had enough surface
area for a single indentation test to be performed.

The data associated with each test were manipulated
25 using standard spreadsheet software and used to calculate

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the hardness, *H*, using the following equation:

$$H[N/mm^2] = \frac{F_{max}[N]}{A_p[mm^2]}$$

where F_{max} is the peak load and A_p is the projected area

of the indentation remaining on unloading. This area can

5   be calculated geometrically from the plastic indentation

depth. This is slightly less than the total penetration

depth measured under load because of elastic deformation

of the sample. The plastic indentation depth is

calculated from a graph of the unloading-force-versus-

10 total-penetration-depth. The initial slope of this

unloading data depends on the initial elastic recovery of

the sample. The plastic indentation depth is estimated

from an intercept between the zero force axis and a

straight line drawn at a tangent to the initial part of

15 the unloading slope.

Similar hardness measurements were also done using a

desktop *Instron Universal Testing Machine* (Model 5566)

fitted with a 10 N load cell, and the data analysis

20 performed in the same way.

iii) Deposition and whiteness of deposit

Another test of the properties of a composition is the amount of the composition which is delivered onto a surface when the composition is drawn across that surface

5   (representing the application of a stick product to human skin). To carry out this test of deposition, a sample of the composition with standardised shape and size is fitted to apparatus which draws the sample across a test surface under standardised conditions. The amount

10 transferred to the surface is determined as an increase in the weight of the substrate to which it is applied. If desired the colour, opacity or clarity of the deposit may subsequently be determined.

15   A specific procedure for such tests used apparatus to apply a deposit from a stick onto a substrate under standardised conditions and then measures the mean level of white deposits using image analysis.

20 The substrates used were

a: 12 x 28cm strip of grey abrasive paper (3M™ P800 WetorDry™ Carborundum paper)

b: 12 x 28cm strip of black Worsted wool fabric.

25   The substrates were weighed before use. The sticks

were previously unused and with domed top surface
unaltered.

The apparatus comprised a flat base to which a flat
5   substrate was attached by a clip at each end. A pillar
having a mounting to receive a standard size stick barrel
was mounted on an arm that was moveable horizontally
across the substrate by means of a pneumatic piston.

10   Each stick was kept at ambient laboratory
temperature overnight before the measurement was made.
The stick was advanced to project a measured amount from
the barrel. The barrel was then placed in the apparatus
and a spring was positioned to biassed the stick against
15   the substrate with a standardised force. The apparatus
was operated to pass the stick laterally across the
substrate eight times. The substrate was carefully
removed from the rig and reweighed.

20   Whiteness of Deposit
The deposits from the previous test were assessed
for their whiteness after an interval of 24 hours
approximately.

25   This was done using a Sony XC77 monochrome video

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camera with a Cosmicar 16mm focal length lens positioned
vertically above a black table illuminated from a high
angle using fluorescent tubes to remove shadowing. The
apparatus was initially calibrated using a reference grey
5   card, after the fluorescent tubes had been turned on for
long enough to give a steady light output. A cloth or
Carborundum paper with a deposit thereon from the
previous test was placed on the table and the camera was
used to capture an image. An area of the image of the
10 deposit was selected and analysed using a Kontron IBAS
image analyser. This notionally divided the image into a
large array of pixels and measured the grey level of each
pixel on a scale of 0 (black) to 255 (white). The
average of the grey intensity was calculated. This was a
15 measure of the whiteness of the deposit, with higher
numbers indicating a whiter deposit. It was assumed that
low numbers show a clear deposit allowing the substrate
colour to be seen.

20   It has been found desirable to carry out deposition
of a standard stick composition, and determine the
whiteness of the deposit, as a control.

iv) Light transmission

25   The translucency of a composition may be measured by

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placing a sample of standardised thickness in the light

path of a spectrophotometer and measuring transmittance,

as a percentage of light transmitted in the absence of

the gel.

5

We have carried out this test using a dual-beam

spectrophotometer. The sample of composition was poured

hot into a 4.5 ml cuvette made of polymethylmethacrylate

(PMMA) and allowed to cool to an ambient temperature of

10   20-25°C. Such a cuvette gives a 1 cm thickness of

composition. Measurement was carried out at 580 nm, with

an identical but empty cuvette in the reference beam of

the spectrophotometer, after the sample in the cuvette

had been held for 24 hours. We have observed that a

15   composition which gives a transmittance of as little as

1% in this test is perceived by eye as "translucent". If

a stick is made from a composition with 3% transmittance,

it is possible to see cavities made by boring beneath the

surface of the sample. By contrast, a conventional stick

20   structure with stearyl alcohol is so opaque that it is

impossible to see beneath its surface. A transmittance

measured at any temperature in the range from 20-25°C is

usually adequately accurate, but measurement is made at

22°C if more precision is required. In a number of

25   preferred examples we have achieved a transmittance of

20% or above.

Preparation

5   Compositions of this invention can be produced by

conventional processes for making suspension or emulsion

solids or soft-solids. Such processes involve forming a

heated mixture of the composition at a temperature which

is sufficiently elevated that all the esterified

10   saccharide structurant dissolves, pouring that mixture

into a mould, which may take the form of a dispensing

container, and then cooling the mixture whereupon the

structurant solidifies into a network of interconnected

fibres extending through the water-immiscible liquid

15   phase.

In a suitable procedure for making emulsion

formulations, a solution of the esterified structurant in

the water-immiscible liquid phase is prepared at an

20   elevated temperature just as for suspension sticks. If

any emulsifier is being used, this is conveniently mixed

into this liquid phase. Separately an aqueous or

hydrophilic disperse phase is prepared by introduction of

antiperspirant active into the liquid part of that phase

25   (if this is necessary; antiperspirant actives can

sometime be supplied in aqueous solution which can be

utilised as is). This solution of antiperspirant active

which will become the disperse phase is preferably heated

to a temperature similar to that of the continuous phase

5   with structurant therein, but without exceeding the

boiling point of the solution, and then mixed with the

continuous phase. Alternatively, the solution is

introduced at a rate which maintains the temperature of

the mixture. If necessary a pressurised apparatus could

10 be used to allow a higher temperature to be reached, but

with the structurant materials of this invention this is

usually unnecessary. After the two phases are mixed, the

resulting mixture is filled into dispensing containers,

typically at a temperature 5 to 30°C above the setting

15 temperature of the composition, and allowed to cool.

Cooling may be brought about by nothing more than

allowing the container and contents to cool. Cooling may

be assisted by blowing ambient or even refrigerated air

20 over the containers and their contents.

55

EXAMPLES

The examples below were prepared using a number of
materials set out with their proprietary names in the

5   following list. All temperature are in degrees Celsius.
Refractive indices were measured at 25°C.

1)   octamethyl cyclotetrasiloxane (Volatile cyclic
silicone also known as a cyclomethicone; DC 245
from Dow Corning)

10   2)   decamethyl cyclopentasiloxane (Volatile cyclic
silicone also known as a cyclomethicone; DC 345
from Dow Corning)

3 & 4)   Non-volatile silicone fluids
DC 556 and DC 710 (Dow Corning)

15   5)   Polydecene (Silkflo 364NF from Albemarle)

6)   Isostearyl Alcohol (abbreviated to ISA -
Prisorine 3515 from Unichema)

7)   C12-15 alkyl benzoate (Finsolv TN from Fintex)

8)   Mineral Oil (Sirius M70 from Dalton)

20   9)   Polypropyleneglycol 14 butylether (Fluid AP
from Amercol)

10)   Isopropyl myristate (abbreviated to IPM from
Unichema)

11)   Isohexadecane (Permethyl 101A from

25   Presperse Inc)

12)   Isoeicosane (Permethyl 102A from
         Presperse Inc).

13)   Cetyl dimethicone copolyol (Abil EM90
         emulsifier from Th. Goldschmidt)

14)   C20 - C40 alcohols (Unilin 425 from Petrolite)

15) 50% aqueous solution of Al/Zr pentachlorohydrate
     (Zirkonal 50 from Giulini)

16)   Al/Zr Tetrachlorohydrex glycine complex 30% in
         propylene glycol (WA2Z 8106 from Westwood)

17)   Al/Zr tetrachlorohydrex glycine complex (AZG
         375 from Summit)

18)   Glycerol (from Aldrich)

19)   Propylene glycol (from Fisons)

20)   N-lauryl-L-glutamic acid di-n-butylamide (GP-1
         from Ajinomoto)

21) Bis-phenylpropyldimethicone, a non-volatile silicone
     fluid (SF 1555 from G E Silicones)

22) Polyglyceryl polyricinolate (Quest PGPR)

23) 1-octyldodecanol (Eutanol G from Henkel/Cognis)

24) Hydrogenated polyisobutene (Panalene-L-14E from
     Amoco)

25) Hydrogenated polyisobutene (Fancol 800 from Fanning
     Corporation)

26) Polyglyceryl-3-diisostearate (Lameform TGI from
     Henkel/Cognis)

27) Polyglyceryl-2-dipolyhydroxystearate (Dehymuls PGPH from Henkel/Cognis)

28) Polyalpha Olefins (Puresyn 4 from Mobil Chemical)

5   29) Ceteareth 20 (Eumulgin B2 from Henkel)

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Example 1

The enthalpy of gelation was measured for a number

of structuring agents in three liquids. In each case the

5   gels are made to contain 7 to 7.5 wt% of the structurant

in the liquid.

A sample gel, weighing between 18 and 22 mg was

placed in a stainless steel calorimeter capsule, which

10   was sealed with an elastomeric O-ring. The capsule was

placed in the DSC at room temperature and heated at

10K/minute to 150°C, held at 150°C for 60 seconds and

cooled at 2K/minute to -50°C.

15   The procedure was repeated with DC 345 alone. The

data recorded for DC 345 was subtracted from the data for

the gel, so that the gel formation appears a departure

from a flat baseline. The gelation enthalpy was

calculated as the area between the peak and the baseline.

20

Values of enthalpy (in kJ/mole) were obtained as set

out in the following table

59

Structurant	Liquid		
	DC 345	DC 345:ISA (80:20 ratio by weight)	Isostearyl alcohol (ISA)
α-cellobiose octa-octadecanoate		360	
α-cellobiose octa-dodecanoate		108	
α-cellobiose octa-undecanoate		117	
α-cellobiose octa-decanoate	84.7	94.6	
α-cellobiose octa-nonanoate	65	58	77
α-cellobiose octa-octanoate		57.8	
12-hydroxystearic acid		40	
β-sitosterol and Oryzanol in 1:1 mole ratio		22	
N-lauroyl glutamic acid di-n-butylamide (GP-1)		11	25
Lanosterol	27	7	

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Example 2 (Comparative)

Gels were prepared with lanosterol by a standard procedure in which the ingredients of the gel were placed in a 30ml glass bottle together with a magnetic stirrer bar. The mixture was stirred and heated until all the lanosterol had dissolved. The bottle was then removed from the heat, the stirrer bar taken out and the contents of the jar left to cool to room temperature.

The following was observed:

Lanosterol was found to dissolve at 10.0 wt% in Finsolv TN at 83°C. After cooling to room temperature for 1 hours a hard, transparent gel was obtained. However the gel was found to be unstable at room temperature: large crystalline lumps appeared within hours and spread throughout the entire gel leading to is collapse.

Lanosterol was found to dissolve at 5.0 wt% in 80:20 (wt%) DC 345: Finsolv TN at 85°C. After cooling to room temperature for 1 hour a hard, translucent gel was obtained. However the gel was found to be unstable at room temperature: large crystalline lumps developed after 1 week.

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Example 3 (Comparative)

Unsuccessful attempts were made to prepare composi-
tions as set out in the table below, using N-lauroyl
5   glutamic acid di-n-butylamide (GP-1) as structurant

The two compositions would have been emulsions where
the disperse phase would be a solution of antiperspirant
active in water (Zirkonal 50 is a 50% aqueous solution of
10 antiperspirant active).

Example no	3a	3b
	Emulsion	Emulsion
Continuous phase		
GP-1 (20)	3.5%	5%
DC 345 (2)	39%	43%
Isostearyl alcohol (6)		11%
Finsolv TN (7)	16.5%	
Abil EM90 (13)	1%	1%
Disperse Phase		
Zirkonal 50 (15)	40%	40%
Continuous Phase Data		
Temp at which all the GP-1 had dissolved	122□C	119□C
Temperature at which the continuous phase gelled	116□C	99□C

In each case the components of the continuous phase

were placed in a beaker and the mixture heated with
stirring on a hot plate until all the GP-1 structurant
dissolved. The temperature at which it dissolved is
shown in the table above.

5

The intention was then to cool the mixture, while
still stirring gently to about 85-90□C in order to add
the components of the disperse solid or liquid phase. In
all cases the continuous phase gelled at a temperature

10   (shown in the table) above or very close to 100°C, which
was too high for safe addition of the disperse phase in
an open laboratory.

Safe preparation at this high temperature would have

15   required special measures such as pressurised apparatus.

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Example 4

Cellobiose was esterified with nonanoic acid to yield the fully esterified product in the form of its α-anomer following a procedure generally as described in

5   Takada et al, Liquid Crystals, Volume 19, page 441 (1995).

The following materials were used:

β-D-cellobiose, 20 grams, 0.058 moles

10   Nonanoic acid, 591.6 grams, 3.74 moles

Trifluoroacetic anhydride, 297.6 grams, 1.42 moles.

These materials were obtained from Acros Organics - Fisher Scientific.

15

Into a 2 litre flange pot equipped with an overhead stirrer, water condenser and addition inlet was placed the nonanoic acid together with the trifluoroacetic anhydride. The resultant clear mixture was stirred up and heated to

20   100°C using a silicone oil bath and temperature probe. During heating it was noted that the colour of the reaction mixture darkened and developed a dark brown tinge. After allowing the mixture to stir for one hour at 100°C, the cellobiose was slowly added via a solid powder funnel to the

25   dark activated solution, and a dirty brown suspension was

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formed which re-dissolved forming a clear black solution within 10-20 minutes.

5   The reaction flask was then maintained at 100°C for a total of 6 hours then cooled down to ambient laboratory temperature. Next the contents of the flask were transferred into 2 litres of methanol containing 10% de-ionised water in an ice-cooled 5 litre beaker. Immediately an off-white solid precipitate came out of
10   solution, this was filtered off and collected. The crude solid was recrystallised a total of 4 times from a tetrahydrofuran/methanol solution producing a white solid product.

15   The product was obtained in a quantity of 31.5 g which was a 37% yield. It had a melting point of 110°C. The infra-red spectrum showed an absorption peak at 1739 cm^{-1} for the ester carbonyl group. The amount of free acid could be determined from its absorption peak at 1705 cm^{-1}.
20

The n.m.r. spectrum showed the amount of cellobiose which was fully esterified to be 93.5% and showed the proportions of product which were the α- and β-anomers, (93.5% α-anomer).

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Other esters of cellobiose were prepared in the same
way. Samples of esterified cellobiose prepared as above
were used to gel various water-immiscible liquids and
mixtures of liquids. The procedure was as follows:

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0.5 grams esterified cellobiose and 9.5 grams of the
liquid (or other proportions to give a total of 10 grams) were
weighed directly into a 15 gram or 30 gram glass jar. A small
magnetic follower was placed in the jar which was then placed
10 on a hot plate. It was stirred and heated until all of the
esterified cellobiose had dissolved in the liquid. This
"dissolution temperature" was noted. The jar was then removed
from the hot plate, the stirrer was removed from the hot
liquid in the jar. A thermometer was placed in the liquid and
15 the contents of the jar were then left undisturbed to cool.
The gelling temperature, i.e. the temperature at which the
contents gelled, was noted. The jar was left to stand for
24 hours and then the contents of the jar were inspected
visually, pressed with a probe and classified
20 qualitatively according to their appearance as a soft,
medium or hard gel. The clarity or otherwise of the gel
was noted. In most instances the gel was remelted, the
remelting temperature was noted, and some of the melt was
poured into a plastic (polymethylmethacrylate) cuvette and
25 allowed to cool back to ambient laboratory temperature so

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that the gel reformed in the cuvette. The transmittance of light through the 1cm thickness of gel in the cuvette was determined at a wave length of 580 nm using an ultraviolet/visible spectrophotometer.

5

The following tables show the water-immiscible liquids which were used, the percentage of esterified cellobiose structurant used to gel the liquid, the dissolution temperature, the gelling temperature, the visual appearance of the gel, the remelt temperature and the percentage

10 light transmittance (denoted as %T) through 1cm of the gel at 580nm.

Gelling with α-cellobiose octa-octanoate("CB8" $R = COC_7H_{15}$)						
Liquid	% CB8	Diss Temp	Gel Temp	Remelt Temp	% T	Visual appearance of gel
ISA (6)	5	41	30	41		Hard & transparent -> crystal growth
	10	41	35			Hard & translucent -> crystal growth
DC 345 (2)	5	48	41	50	17	Hard & transparent/ translucent
	10	53	50			Hard & opaque
DC 556 (3)	5	48	30	45	49	Hard & transparent
	10	49	35			Hard & transparent
Silkflo 364 NF (5)	5	53	45	51	22	Hard & transparent
	10	55	50			Hard & opaque

Gelling with α-cellobiose octa-nonanoate ("CB9")						
Liquid	% CB9	Diss Temp	Gel Temp	Remelt Temp	% T	Visual appearance of gel
ISA (6)	5	57	25	46	78	Medium/hard & transparent
DC 345 (2)	5	62	42	60	15	Hard & transparent/ translucent
DC 566 (3)	5	69	29	52	81	Hard & transparent
Silkflo 364NF (5)	5	71	40	55	78	Hard & transparent
Fluid AP (9)	5	82	38	55	37	Soft/medium & transparent
DC 345 : Fluid AP 80 : 20 wt ratio	5	68	28	54	39	Soft/medium & transparent
DC 710 (4)	5	82	48	62	11	Medium & translucent
DC 710 : DC 345 60 : 40 wt ratio	5	74	33	60	4	Hard & translucent

Gelling with α-cell biose cta-decanoate ("CB10" R = COC₉H₁₉)						
Liquid	% CB10	Diss Temp	Gel Temp	Remelt Temp	% T	Visual appearance of gel
Finsolv TN (7)	5	72	25	38		Very soft & Transparent gel
ISA (6)	5	72	25	47	46	Medium & transparent
	7	68	25	52		Hard & translucent
	10	76	30			Medium & transparent
DC 345 (2)	5	85	62	71	0.02	Hard & translucent/ opaque
	7	84	65	59		Hard & opaque
DC 556 (3)	3	79	46	59		Medium & transparent
	5	n/d	50	52	2	Medium/hard & translucent
	7	74	40	67		Hard & translucent
Fluid AP (9)	3	85	35	60		Medium & transparent
	5	82	33	51		Medium & transparent
	7	78	51	53	3	Medium & translucent
	10	84	45			Medium & translucent/ opaque
DC 345 : Fluid AP 80 : 20 wt ratio	5	73	25	55	<0.01	Medium & translucent/ opaque
	7	82	36	49		Hard & opaque
	10	83	41			Hard & opaque
DC 710 (4)	5	100	80	80	0.15	Medium & opaque
DC 710 : DC 345 60 : 40 wt ratio	5	92	65	65	1	Medium & translucent/opaque trans

Gelling with α-cellobi se cta-dodecanoate ("CB12" R = COC₁₁H₂₃)						
Liquid	% CB12	Diss Temp	Gel Temp	Remelt Temp	% T	Visual appearance of gel
ISA (6)	5	54	30	48	12	Soft & transparent/translucent
DC 345 (2)	5	50	48	50	0.17	Soft & opaque
DC 556 (3)	5	60	35	48	17	Medium & transparent/translucent
Silkflo 364 NF (5)	5	53	45	55	3	Medium & transparent
Fluid AP (9)	5	63	43	55	4	Soft & transparent/translucent
DC 345: Finsolv TN 80 : 20 wt ratio	5	65	29	42	3	soft & translucent
DC 345 : Fluid AP 80 : 20 wt ratio	5	63	42	50	0.25	Soft/medium & opaque
DC 710 (4)	5	65	57	65	1	Medium & opaque
DC 710 : DC 345 60 : 40 wt ratio	5	65	48	55	39	Soft & transparent

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Gelling with α-cellobiose octa-octadecanoate ("CB18" R = COC$_{17}$H$_{35}$)						
Liquid	% CB18	Diss Temp	Gel Temp	Remelt Temp	% T	Visual appearance of gel
Finsolv TN (7)	5	68	47	60	0.12	very soft & opaque
	7	68	47			
IPM (10)	5	68	50	59	0.01	very soft & opaque
	7	72	50			very soft & opaque
ISA (6)	5	68	58	62	0.03	very soft & opaque
	7	70	61			soft & opaque
DC 345 (2)	5	85	82	80	<0.01	soft & opaque
	7	87	86			soft & opaque
	10	85	84			medium & opaque
DC 556 (3)	5	77	76	75	0.08	soft & opaque
	7	83	79			soft & opaque
	10	83	79			medium & opaque
Silkflo 364 NF (5)	5	72	66	75	0.11	medium & opaque
	7	72	68			medium & opaque
	10	79	69			medium & opaque
Fluid AP (9)	5	78	76	78	0.01	soft & opaque
	7	82	77			medium & opaque
	10	82	81			soft & opaque

It can be seen from the above table that the gelation temperatures were low. The remelt temperatures were generally below 80°C and most of the compositions could be prepared without any need to exceed 85°C.

Example 5

Opaque emulsion sticks were prepared with formula-
tions as set out in the table below.

To prepare these sticks, the cyclomethicone was
mixed with the other organic liquids (if any) including
the cetyl dimethicone copolyol which functioned as an
emulsifier (silicone surfactant) and the mixture was
heated with gentle stirring to a temperature 5 to 10°C
above the temperature at which the structurant had been
found to dissolve in a preliminary test. The esterified
cellobiose was then added and allowed to dissolve.

The disperse phase (also referred to as internal
phase) was an aluminium zirconium active dissolved in
water or in a mixture of a polyol and water. This
disperse phase was pre-heated to the same temperature as
the organic oils containing the esterified cellobiose and
added slowly to them over a period of one minute while
mixing with a Silverson mixer. After addition was
complete the formulation was mixed at higher speed for
five minutes. Stirring speed was then reduced for a further
one minute after which the mixture was poured into stick
barrels and allowed to cool undisturbed to ambient laboratory
temperature. The sticks were tested by penetrometer, by
texture analyser and for whiteness of deposits, in each
instance by the test procedures given earlier. All of the
sticks were opaque although without the chalky white

appearance of a commercial white stick (CWS) structured with stearyl alcohol and castor wax whose test results are given at the right of the table.

Examples	5.1	5.2	5.3	CWS
	% by weight			
Cyclomethicone DC 245 (1)	18	22.25	21.7	
Polydecene (5)	22.75	27.5	27.4	
PPG-14 Butyl Ether (9)	4.5	5.5	5.4	
Cellobiose octa-nonanoate	3.75	3.75	4.5	
Cetyl Dimethicone Copolyol (13)	1	1	1	
Zirkonal 50 (15)	40	40	40	
Water	10	-	-	
	Properties			
Penetration depth (mm)	16.8	17.5	15.7	9.8
Hardness by texture analyser (N/mm²)	0.11	0.10	0.12	-
Whiteness on grey paper 24 hours after deposition	19	16	16	118
Whiteness on black wool 24 hours after deposition	28	28.5	27	186

5

Example 6

Sticks were prepared and tested in accordance with the procedure given in Example 5. The sticks were tested

5   for hardness by texture analyser and/or by penetrometer. They were observed to give deposits of low whiteness, but numerical data were not recorded.

For some sticks in this example the refractive indices of the water-immiscible continuous phase and the polar

10 anti-perspirant active solution were matched sufficiently to give translucent sticks. Some values of transmittance are shown.

Examples	6.1	6.2	6.3	6.4	6.5
	% by weight				
DC245 (1)	44	21.625	21.625	21.625	18
Silkflo364 (5)	-	-	-	21.625	4
Permethyl 102A (12)	—	21.625	-	-	-
SF1555 (21)	-	-	21.625	-	22
Abil EM90 (13)	1	-	-	-	1
Quest PGPR (22)	-	1.75	1.75	1.75	-
Esterified Cellobiose -C9	5	5	5	5	5
Zirkonal 50 (15)	39	40	40	40	40
Glycerol (18)	-	8	9	8.75	10
Water	11	2	1	1.25	-
	Properties				
Penetration depth (mm)	9.3	12	11.3	13	
Hardness by texture analyser (N/mm^2)	0.10	0.12	0.12	0.21	0.13

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Examples	6.6	6.7	6.8	6.9	6.10
	% by weight				
Cyclomethicone DC 245 (1)	7.6	6.8	36.5	1.7	1.25
Isostearyl alcohol (6)	-	-	-	23.3	-
Octyldodecanol (23)	-	-	-	-	23.1
SF1555 (21)	37.43	37.7	7	-	-
Silkflo 364 (5)	-	-	-	16.8	17.65
Esterified Cellobiose -C10	8.12	7.3	7.8	7	7
Cetyl Dimethicone Copolyol (Abil EM90) (13)	1.1	1	1	1	1
Westwood active (16)	43.54	41	42	40	40
Glycerol (18)	-	4.7	5.2	6.8	6.5
Water	2.21	1.5	0.5	3.4	3.5
	Properties				
Matched RI of phases	1.45	1.45	1.46	1.45	1.45
Penetration depth (mm)	9.1	6.9	8.7	8.8	9.1
Hardness by texture analyser (N/mm^2)	0.37	0.03	0.08	0.04	0.19
Transmittance at 580nm (%)	8	3	5	6	5

Examples	6.11	6.12 _	6.13	6.14
	% by weight			
DC245 (1)	12	11.32	-	-
Silkflo 364 (5)	32.5	30.68	39	41.5
Abil EM90 (13)	0.5	0.5	1	1
Esterified Cellobiose -C10	5	7.5	10	7.5
Zirkonal 50 (15)	33	33	-	-
Westwood active (16)	-	-	48.06	48.06
Glycerol (18)	17	17	-	-
Water	-	-	1.94	1.94
	Properties			
Penetration depth (mm)	19	14	7.3	9.6
Hardness by texture analyser (N/mm^2)	0.44	0.07	0.47	0.15

5

Example 7

The procedure of Example 5 was repeated to prepare

a number of emulsion sticks with formulations set out in

the following tables. The continuous and disperse

phases were formulated to have refractive indices which

matched closely at the value given in the tables. These

sticks were tested as before and the properties are also

given in these tables.

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Examples	7.1	7.2	7.3	7.4	7.5	7.6
	% by weight					
Cyclomethicone DC245 (1)	22.625	18.75	25.5	19	26	17.75
Mineral Oil (8)	22.625	-	-	-	-	-
Polydecene (5)	-	22.5	15.75	22	15	22
PPG-14 Butyl Ether (9)	-	4	4	-	-	4.25
Isostearyl Alcohol (6)	-	-	-	4.25	4.25	-
Cellobiose octa-nonanoate	3.75	3.75	3.75	3.75	3.75	5
Cetyl Dimethicone Copolyol (13)	1	1	1	1	1	1
Zirkonal 50 (15)	40	40	40	40	40	40
Glycerol (18)	10	10	7.5	10	7.5	10
Water	-	-	2.5	-	2.5	-
	Properties					
Matched refractive index of phases	1.43	1.43	1.425	1.435	1.425	1.43
penetration depth (mm)	19.3	18.5	17.3	24.7	23.6	12.4
Hardness by texture analyser (N/mm^2)	0.11	0.12	0.08	0.07	0.06	0.17
Whiteness on grey paper 24 hours after deposition	-	15	16	18	19	16
Whiteness on black wool 24 hours after deposition	-	24	28	25	30	26
Transmittance at 580nm	-	38%	33%	41%	35%	51%

Examples	7.7	7.8	7.9	7.10	7.11
	% by weight				
Cyclomethicone DC245 (1)	16.75	18	14.02	28.4	4.5
Polydecene (5)	20.75	22.75	17.72	13.1	50.75
PPG-14 Butyl Ether (9)	4	4.5	3.51	3.75	-
Cellobiose octa-nonanoate	7.5	3.75	3.75	3.75	3.75
Cetyl Dimethicone Copolyol (13)	1	1	1	1	1
Zirkonal 50 (15)	40	-	40	40	-
Glycerol (18)	10	4	17.5	6.25	12
Water	-	14	2.5	3.75	8
Propylene glycol (19)	-	12	-	-	-
AZG 375 (17)	-	20	-	-	20
	Properties				
Matched RI of phases	1.43	1.43	1.43	1.42	1.45
penetration depth (mm)	11	14.5	14.9	15.1	14.8
Hardness by texture analyser (N/mm^2)	0.29	0.11	0.14	0.13	0.11
Whiteness on grey paper 24 hours after deposition	17	20	18	21	16
Whiteness on black wool 24 hours after deposition	25	28	25	31	19
Transmittance at 580nm	48%	82%	65%	30%	72%

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Examples	7.12	7.13	7.14	7.15	7.16
	% by weight				
Cyclomethicone DC245 (1)	41.85	35.4	10.04	10.64	6.96
Permethyl 101A (11)	2.15	-	-	-	-
Permethyl 102A (12)	-	8.6	-	-	-
Polydecene (5)	-	-	12.7	13.45	8.8
PPG-14 Butyl Ether (9)	-	-	2.51	2.66	1.74
Cellobiose octa-nonanoate	5	5	3.75	2.25	1.5
Cetyl Dimethicone Copolyol (13)	1	1	1	1	1
Zirkonal 50 (15)	40	40	52.71	52.71	60.24
Glycerol (18)	0.75	4.5	17.29	17.29	19.76
Water	9.25	5.5	-	-	-
	Properties				
Matched refractive index of phases	1.40	1.41	1.43	1.43	
penetration depth (mm)	13.5	13.2	12.0	16.8	
Hardness by texture analyser (N/mm²)	0.16	0.15	0.13	0.07	
Whiteness on grey paper 24 hours after deposition	59	61	24	24	
Whiteness on black wool 24 hours after deposition	122	24	14.9	16.2	
Transmittance at 580nm	2.7%	5%	33%	73%	

Example 8

5   The procedure of Example 5 was repeated to prepare a
number of emulsion sticks with formulations set out in
the following tables. As in Example 7, the continuous
and disperse phases were formulated to have refractive
indices which matched closely at the value given in the
10   tables. The sticks were tested for hardness by texture
analyser and/or by penetrometer. They were observed to
give deposits-of low whiteness, consistent with their
good clarity, but numerical data were not recorded.

15   The refractive indices ·of sample quantities of the
water-immiscible liquid mixture and the antiperspirant
active solutions were checked before making the sticks.
If necessary their formulations were modified very
slightly to optimise the refractive index match.

Examples	8.1	8.2	8.3	8.4	8.5	8.6
	% by weight					
Permethyl 102A (12)	41.36	-	-	-	-	-
Panalene L-14E (24)	-	-	22	-	-	-
Fancol 800 (25)	-	-	-	22	22	-
Puresyn 4 (28)	-	-	-	-	-	22
DC245 (1)	2.64	11.4	22	22	22	22
SF 1555 (21)	-	34.1	-	-	-	-
Esterified cellobiose C9	5	4.9	5	5	5	5
Abil EM90 (13)	1	1	1	1	1	1
Zirkonal 50 (15)	-	-	40	40	36.6	40
Westwood active (16)	50	48.6	-	-	-	-
Glycerol (18)	-	-	9.35	7.5	13.4	8.75
Water	-	-	0.65	2.5	-	1.25
	Properties					
Matched RI of phases (at 25□C)	1.46	1.45	1.431	1.425	1.437	1.429
penetration depth (mm)	9	11	10.5	12.1	7.9	8.8
Hardness by texture analyser (N/mm²)	0.11	0.11	0.13	0.12	0.11	0.10
Transmittance at 580nm (%)	68	70	40	6	70	37

Examples	8.7	8.8	8.9	8.10	8.11
	% by weight				
DC245 (1)	22	22.25	22.25	21.625	-
DC556 (3)	22	-	-	-	-
Silkflo364 (5)	-	-	-	-	44
Permethyl 102A (12)	-	22.25	-	-	-
Panalene-L-14E (24)	-	-	-	21.625	-
SF1555 (21)	-	-	22.25	-	-
Abil EM90 (13)	1	0.5	0.5	-	1
Lameform TGI (26)	-	-	-	0.875	-
Dehymuls PGPH (27)	-	-	-	0.875	-
Esterified cellobiose C9	5	5	5	5	5
Zirkonal 50 (15)	40	40	40	40	50
Glycerol (18)	9	8	9	9.8	-
Water	1	2	1	0.2	-
	Properties				
Matched RI of phases (at 25□C)	1.428	1.43	1.43	1.43	1.46
Penetration depth (mm)	9.0	11	11	10.5	9
Hardness by texture analyser (N/mm²)	0.10	0.09	0.16	0.13	0.13
Transmittance at 580nm (%)	40	22	33	36	24

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Examples	8.12	8.13	8.14	8.15	8.16	8.17
			% by weight			
DC245 (1)	-	-	-	22	22	18
Silkflo364 (5)	44	-	-	-	-	5.3
Permethyl 102A (12)	-	44	-	22	-	-
Panalene-L-14E (24)	-	-	44	-	-	-
SF1555 (21)	-	-	-	-	22	-
Octyldodecanol (23)	-	-	-	-	-	21.9
Abil EM90 (13)	1	1	1	1	1	1
Esterified Cellobiose C9	5	5	5	5	5	5
Zirkonal 50 (15)	18	21.5	12	-	-	37.8
AZG-375 (17)	-	-	-	25	25	-
Glycerol (18)	32	28.5	38	0.6	2.5	11
Water	-	-	-	24.4	22.5	-
			Properties			
Matched refractive index of phases (at 25□C)	1.45	1.45	1.46	1.43	1.43	1.43
Penetration depth (mm)	9	9	7	9	8	-
Hardness by texture analyser (N/mm²)	0.13	0.15	0.20	-	0.21	0.12
Transmittance at 580nm (%)	74	46	82	53	41	24

Example 9

The procedure of Example 5 was used to prepare a number of emulsion sticks with formulations set out in the following table. These sticks did not contain antiperspirant active. They would be useful as moisturizing stick or lip salve and their compositions could be used as the basis for other, probably opaque, cosmetic stick products. The continuous and disperse phases were formulated to have refractive indices which matched closely at the values given in the table, but evaporative losses during processing interfered with this. The sticks were tested for hardness by texture analyser and/or by penetrometer.

Examples	9.1	9.2	9.3	9.4
	% by weight			
DC245 (1)	22	22	16.72	19.36
Silkflo364 (5)	22	-	27.28	-
SF1555 (21)	-	22	-	24.64
Abil EM90 (13)	1	1	1	1
Esterified Cellobiose C9	5	5	5	5
Glycerol (18)	33.5	37.5		-
Water	16.5	12.5	-	-
Propylene Glycol (19)	-	-	50	50
	Properties			
Matched RI of phases (at 25□C)	1.42	1.43	1.43	1.43
Penetration depth (mm)	9	9	-	10
Hardness by texture analyser (N/mm²)	0.13	0.15	0.15	-

Example 10

The procedure of Example 5 was used to prepare translucent emulsion sticks with the formulation below in which the structurant is α-cellobiose octa-undecanoate ("CB11"). As in Example 7, the continuous and disperse phases were formulated to have refractive indices which matched closely at the value given. The sticks were tested for hardness by texture analyser and/or by penetrometer. They were observed to give deposits of low whiteness.

Ingredients	percent by weight
DC245 (1)	11
Silkflo 364 (5)	33
Abil EM90 (13)	1
Esterified Cellobiose C11	5
Zirkonal 50 (15)	33
Glycerol (18)	17
Properties	
Matched RI of phases(at 25□C)	1.44
Penetration depth (mm)	16
Hardness by texture analyser (N/mm²)	0.05
Transmittance at 580nm (%)	6

Example 11

The procedure of Example 5 was used to prepare an opaque emulsion stick of the following formulation, which included agents to assist wash-off.

Ingredients	percent by weight
DC245 (1)	16.4
Silkflo 364 (5)	24.6
Abil EM90 (13)	1
Esterified cellobiose C9	5
Zirkonal 50 (15)	40
Glycerol (18)	10
Ceteareth 20 (29)	2.5
C_{20-40} alcohols (14)	0.5

CLAIMS:

1.   A cosmetic composition which is a structured emulsion
comprising

5   i)   a continuous phase containing water-immiscible liquid
          carrier and a fibre-forming structurant present in the
          continuous phase, which is effective to gel the
          composition upon cooling from a temperature at which the
          structurant is in solution in the carrier liquid, and

10 ii)   a disperse phase which is a solution of antiperspirant
          active in water, water-soluble solvent or a mixture of
          them,

characterised in that the structurant has an enthalpy of
gelation in the carrier liquid with a magnitude of at least
15 30 kJ/mole.

2.   A cosmetic composition which is a structured emulsion
comprising

i)   a continuous phase containing water-immiscible liquid
20   carrier and a fibre-forming structurant present in the
          continuous phase, which is effective to gel the
          composition upon cooling from a temperature at which the
          structurant is in solution in the carrier liquid, and

ii)   a disperse phase which is a solution of antiperspirant
25   active in water, water-soluble solvent or a mixture of

them

characterised in that the structurant is able to gel one or
more of

decamethyl cyclopentasiloxane

5   an 80:20 wt% mixture of decamethyl cyclopentasiloxane
and isostearyl alcohol

isostearyl alcohol

with an enthalpy of gelation in at least one of the liquids
with a magnitude of at least 30 kJ/mole.

10

3.   A composition according to claim 2 wherein the
structurant is able to gel an 80:20 wt% mixture of decamethyl
cyclopentasiloxane and isostearyl alcohol with an enthalpy of
gelation having a magnitude of at least 30 kJ/mole.

15

4.   A composition according to claim 2 wherein the
structurant is able to gel an 80:20 wt% mixture of decamethyl
cyclopentasiloxane and isostearyl alcohol with an enthalpy of
gelation having a magnitude of at least 45 kJ/mole.

20

5.   A composition according to any one of claims 1 to 4
wherein the disperse phase contains a diol or polyol.

6.   A composition according to any one of claims 1 to 5

which contains from 0.1% to 10% by weight of a nonionic emulsifier.

7.   A composition according to any one of the preceding claims which does not contain more than 5% by weight of any fatty alcohol which is solid at 20°C.

8.   A composition according to any one of the preceding claims which does not contain more than 2% by weight of any fatty alcohol which is solid at 20°C.

9.   A composition according to any one of claims 1 to 8 which does not contain more than 8% by weight of ethanol or any monohydric alcohol with a vapour pressure above 1.3 kPa at 22°C.

10.   A composition according to any one of the preceding claims wherein the water-immiscible liquid carrier contains a volatile silicone and optionally a non-volatile silicone and/or a non-silicone hydrophobic organic liquid selected from hydrocarbons, hydrophobic aliphatic esters, aromatic esters, hydrophobic alcohols and hydrophobic ethers.

11.   A composition according to any one of the preceding claims wherein the water-immiscible carrier liquid contains

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silicone oil in an amount which is at least 10% by weight of the composition.

12. A composition according to any one of the preceding claims containing from 0.1 to 12% by weight of the structurant.

13. A composition according to any one of the preceding claims which is an antiperspirant composition comprising an antiperspirant active dissolved in said disperse phase.

14. A composition according to claim 13 wherein the antiperspirant active comprises an aluminium and/or zirconium halohydrate, an activated aluminium and/or zirconium halohydrate, or an aluminium and/or zirconium complex or an activated aluminium and/or zirconium complex.

15. A composition according to claim 14 wherein the antiperspirant active is a halohydrate or complex in which aluminium and zirconium are both present.

16. A composition according to any one of claims 13 to 15 wherein the proportion of antiperspirant active is from 5 to 40% by weight of the composition.

17. A composition according to any one of the preceding claims in which a firm gel such that a penetrometer needle with a cone angle of 9 degrees 20 minutes, drops into the gel for no more than 30 mm when allowed to drop under a total

5 weight of 50 grams for 5 seconds.

18. A composition according to any one of the preceding claims which is translucent or transparent.

10 19. A composition according to any one of the preceding claims which has at least 1%, and preferably at least 3%, light transmittance at 580 nm through a 1 cm thickness of the composition at 22°C.

15 20. A composition according to any one of claims 1 to 19, accommodated within a dispensing container.

21. A cosmetic product comprising a composition according to any one of claims 1 to 19 and a dispensing container which

20 accommodates the composition and has at least one aperture for delivery of the contents of the container and means for urging the contents of the container to the said aperture or apertures.

25 22. A product according to claim 21 wherein the composition

is in the form of a stick and the container has an open end

at which an end portion of the stick of composition is

exposed for use.

5   23.   A process for the production of a composition according

to any one of claims 1 to 19 comprising, not necessarily in

any order,   the steps of

•   incorporating a structurant into a water-immiscible

liquid carrier

10   •   mixing the liquid carrier with a disperse liquid phase,

•   heating the liquid carrier or a mixture containing it to

an elevated temperature at which the structurant is

soluble in the water-immiscible liquid carrier,

followed by cooling or permitting the mixture to cool to a

15   temperature at which it is thickened or solidified.

24.   A process according to claim 23 which includes a step of

pouring the mixture at elevated temperature into a dispensing

container and allowing it to cool therein so as to produce a

20   product according to claim 21 or claim 22.

25.   A method for preventing or reducing perspiration on

human skin comprising topically applying to the skin a com

position according to any one of claims 1 to 19.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: STRUCTURED COSMETIC COMPOSITIONS

(57) Abstract: A cosmetic composition is a structured emulsion of a continuous phase containing water-immiscible liquid carrier plus a structurant, and a disperse phase which is a solution of antiperspirant active in a more polar, probably aqueous, solvent. The structurant is a material which forms a network of fibres in the continuous phase, thereby gelling it. The structurant has an enthalpy of gelation in the carrier liquid or a test liquid with a magnitude of at least 30 kJ/mole. This minimum enthalpy of gelation facilitates processing at conveniently accessible temperatures and promotes stability.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 00/01236

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7   A61K7/32   A61K7/34   A61K7/38   A61K7/48

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7   A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data, EMBASE, MEDLINE, BIOSIS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 635 165 A (PANITCH MAXIMO M) 3 June 1997 (1997-06-03) abstract column 1, line 6 - line 22 column 3, line 55 - line 60 column 4, line 40 -column 5, line 38 column 6, line 6 -column 8, line 14 column 8, line 50 - line 61 column 9, line 40 -column 11, line 15 column 11, line 38 - line 55 column 13, line 38 -column 14, line 24 claims --- -/--	1,2, 7-17,20, 23-25

[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family.

Date of the actual completion of the international search	Date of mailing of the international search report
28 July 2000	0 4 12 00

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Cielen, E

Form PCT/ISA/210 (second sheet) (July 1992)

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page 1 of 2

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 265 878 A (KEIL JOSEPH W) 5 May 1981 (1981-05-05) cited in the application abstract column 1, line 66 -column 3, line 45 column 4, line 25 - line 53 column 7, line 21 - line 40 column 7, line 52 -column 8, line 12 column 8, line 61 -column 9, line 5 column 9, line 57 -column 10, line 26 claims ---	1,6, 9-11, 13-16, 20,23-25
A	NOBOHIRO IDE, TAKESHI FUKUDA AND TAKEAKI MIYAMOTO: "GELATION OF FULLY ACYLATED CELLOBIOSE IN ALKANE SOLUTION" BULL. CHEM. SOC. JPN, vol. 68, 1995, pages 3423-3428, XP002127501 the whole document ---	
A	TAKADA A. ET AL.: "DISCOTIC COLUNMAR LIQUID CRYSTALS IN OLIGOSACCHARIDE DERIVATIVES III. ANOMERIC EFFECTS ON THE THERMO-MESOMORPHIC PROPERTIES OF CELLOBIOSE OCTA-ALKANOATES" LIQUID CRYSTALS, vol. 19, no. 4, 1995, pages 441-448, XP000545756 the whole document ---	
A	TERECH PIERRE AND WEISS RICHARD G: "Low Molecular Mass Gelators of Organic Liquids and the Properties of Their Gels" CHEM. REV., vol. 97, 1997, pages 3133-3159, XP002127859 cited in the application page 3154, line 8 - line 17 page 3156, line 53 - line 55 -----	

INTERNATIONAL SEARCH REPORT

Box I   Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II   Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-20, 23-25 (see annexed sheet)

Remark on Protest   ☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet (1)) (July 1998)

FURTHER INFORMATION CONTINUED FROM   PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-20, 23-25

    1.1. Claims: 1-20,23,24
         A cosmetic composition as claimed and the process for its preparation.

    1.2. Claims: 1-20,25
         A cosmetic composition as claimed and a method for preventing or reducing perspiration on human skin by topically applying such a composition.

2. Claims: 21,22

    An antiperspirant product comprising a dispensing container.

Please note that all inventions mentioned under item 1, although not necessarily linked by a common inventive concept, could be searched without effort justifying an additional fee.

INTERNATIONAL SEARCH REPORT

Information on patent family members

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